

We claim:

1. A method for enhancing the stability of a water-in-oil emulsion, said method comprising the step of pretreating at least a portion of said oil prior to emulsification, said pretreating step comprising at least one of adding a polymer to said oil, biotreating said oil, and photochemically treating said oil.
2. The method of claim 1, wherein said pretreating step comprises adding a polymer to said oil prior to emulsification.
3. The method of claim 2, wherein said polymer is selected from the group consisting of functionalized polymers, functionalizable polymers, mixtures of at least two functionalized polymers, mixtures of at least two functionalizable polymers, and mixtures of at least one functionalized polymer and at least one functionalizable polymer.
4. The method of claim 2, wherein said polymer is added at a treat rate of about 0.01wt% to about 1wt% based on the weight of the oil.
5. The method of claim 2, wherein said method further comprises the addition of at least one sulfonating agent to further enhance the stability of said emulsion.
6. The method of claim 5, wherein said sulfonating agent is added at a treat rate of about 0.1wt% to about 15wt% based on the weight of the oil.
7. The method of claim 5, wherein said sulfonating agent is sulfuric acid.
8. The method of claim 7, wherein said sulfuric acid is added to said oil at a treat rate of about 0.5wt% to about 5.0wt% based upon the weight of said oil.
9. The method of claim 5, further comprising the steps of determining the pH of said water-in-crude oil emulsion following emulsification and if necessary adjusting said pH so that it falls in the range of from about 5.0 to about 7.0.

10. The method of claim 9, wherein said pH of said water-in-crude oil emulsion is adjusted by adding ammonium hydroxide to said emulsion.
11. The method of claim 2, wherein said method further comprises the addition of solid particles to said oil prior to emulsification to further enhance the stability of said emulsion.
12. The method of claim 11, wherein said solid particles are added to said oil at a treat rate of about 0.01wt% to about 10wt% based on the weight of said oil.
13. The method of claim 11, wherein said solid particles are oleophilic solid particles.
- 10 14. The method of claim 1, wherein said pretreating step comprises biotreating said oil prior to emulsification.
15. The method of claim 14, wherein said biotreatment step comprises adding oil-degrading microbes, reactor water and nutrients to said oil.
16. The method of claim 15, wherein said reactor water is added at an oil to reactor water ratio of 1:100 to 1:10.
- 15 17. The method of claim 15, wherein said microbes are added at a rate of about 0.1 wt% to about 5 wt% of microbe inoculum to said oil based on the weight of said reactor water, wherein said inoculum has a colony forming unit of between about  $10^3$  to about  $10^9$ .
- 20 18. The method of claim 15, wherein said nutrients comprise carbon, nitrogen and phosphorus containing nutrients.
19. The method of claim 18, wherein said nutrients comprise a carbon to nitrogen to phosphorus ratio of between about 100:10:1 to about 100:10:0.1.
20. The method of claim 14, wherein said biotreatment step occurs at temperatures of between about 20°C to about 70°C.
- 25

21. The method of claim 14, wherein said biotreatment step occurs in the presence of an air purge.
22. The method of claim 14, wherein said method further comprises the addition of solid particles to said oil prior to emulsification to further enhance the stability of said emulsion.
23. The method of claim 22, wherein said solid particles comprise hydrophobic solid particles.
24. The method of claim 22, wherein said solid particles comprise hydrophilic solid particles.
25. The method of claim 22, wherein said solid particles are added to said oil at a treat rate of about 0.05wt% to about 0.25wt% based on the weight of said oil.
26. The method of claim 1, wherein said pretreatment step comprises photochemically treating at least a portion of said oil prior to emulsification.
27. The method of claim 26, wherein said step of photochemically treating said oil comprises irradiating said oil.
28. The method of claim 27, wherein said step of irradiating said oil comprises exposing said oil to radiation in the range of ultraviolet to visible radiation.
29. The method of claim 27, wherein said step of irradiating said oil comprises exposing said oil to sunlight.
30. The method of claim 26, wherein said photochemical treatment is enhanced by the addition of a dye sensitizer.
31. The method of claim 26, wherein said method further comprises the addition of solid particles to said oil prior to emulsification to further enhance the stability of said emulsion.

32. The method of claim 31, wherein said solid particles are added to said oil before said photochemical treatment step.
33. The method of claim 31, wherein said solid particles are added to said oil after said photochemical treatment step, and before said emulsification.
- 5 34. The method of claim 31, wherein said solid particles comprise hydrophobic solid particles.
35. The method of claim 31, wherein said solid particles comprise hydrophilic solid particles
- 10 36. The method of claim 31, wherein said solid particles are added as a gel comprising solid particles and water.
37. The method of claim 36, wherein said solid particles comprise about 1 wt% to about 30 wt% of said gel based on the weight said water.
38. The method of claim 36, wherein said gel is added to said oil in a treat range of about 5 wt% to about 95 wt% of said gel to said oil.
- 15 39. The method of claim 36, wherein said solid particles are bentonite clay.
40. The method of claim 31, wherein said solid particles are added to said oil at a treat rate of about 0.05wt% to about 2.0wt% based on the weight of said oil.
41. A method for recovering hydrocarbons from a subterranean formation, said method comprising the steps of:
- 20 a) preparing a water-in-oil emulsion by
- 1) obtaining oil to be used in said emulsion,
- 2) pretreating at least a portion of said oil, said pretreating step comprising at least one of adding a polymer to said oil, biotreating said oil, and photochemically treating said oil,
- 25 3) adding water, and

- 4) mixing until said water-in-oil emulsion is formed;  
b) injecting said water-in-oil emulsion into said subterranean formation; and  
c) recovering hydrocarbons from said subterranean formation.
42. The method of claim 41, wherein said pretreating step comprises adding a  
5 polymer to said oil prior to emulsification.
43. The method of claim 42, wherein said polymer is selected from the group  
consisting of functionalized polymers, functionalizable polymers, mixtures of at  
least two functionalized polymers, mixtures of at least two functionalizable  
polymers, and mixtures of at least one functionalized polymer and at least one  
10 functionalizable polymer.
44. The method of claim 42, wherein said polymer is added at a treat rate of about  
0.01wt% to about 1wt% based on the weight of the oil.
45. The method of claim 42, wherein said method further comprises the addition of  
at least one sulfonating agent to further enhance the stability of said emulsion.
- 15 46. The method of claim 45, wherein said sulfonating agent is added at a treat rate  
of about 0.1wt% to about 15wt% based on the weight of the oil.
47. The method of claim 45, wherein said sulfonating agent is sulfuric acid.
48. The method of claim 47, wherein said sulfuric acid is added to said oil at a treat  
rate of about 0.5wt% to about 5.0wt% based upon the weight of said oil.
- 20 49. The method of claim 45, further comprising the steps of determining the pH of  
said water-in-crude oil emulsion following emulsification and if necessary  
adjusting said pH so that it falls in the range of from about 5.0 to about 7.0.
50. The method of claim 49, wherein said pH of said water-in-crude oil emulsion is  
adjusted by adding ammonium hydroxide to said emulsion.

51. The method of claim 42, wherein said method further comprises the addition of solid particles to said oil prior to emulsification to further enhance the stability of said emulsion.
52. The method of claim 51, wherein said solid particles are added to said oil at a treat rate of about 0.01wt% to about 10wt% based on the weight of said oil.
53. The method of claim 51, wherein said solid particles are oleophilic solid particles.
54. The method of claim 41, wherein said pretreating step comprises biotreating said oil prior to emulsification.
- 10 55. The method of claim 54, wherein said biotreatment step comprises adding oil-degrading microbes, reactor water and nutrients to said oil.
56. The method of claim 55, wherein said reactor water is added at an oil to reactor water ratio of 1:100 to 1:10.
57. The method of claim 55, wherein said microbes are added at a rate of about 0.1 wt% to about 5 wt% of microbe inoculum to said oil based on the weight of said reactor water, wherein said inoculum has a colony forming unit of between about  $10^3$  to about  $10^9$ .
- 15 58. The method of claim 55, wherein said nutrients comprise carbon, nitrogen and phosphorus containing nutrients.
59. The method of claim 58, wherein said nutrients comprise a carbon to nitrogen to phosphorus ratio of between about 100:10:1 to about 100:10:0.1.
60. The method of claim 54, wherein said biotreatment step occurs at temperatures of between about 20°C to about 70°C.
61. The method of claim 54, wherein said biotreatment step occurs in the presence of an air purge.
- 25

62. The method of claim 54, wherein said method further comprises the addition of solid particles to said oil prior to emulsification to further enhance the stability of said emulsion.
- 5 63. The method of claim 62, wherein said solid particles comprise hydrophobic solid particles.
64. The method of claim 62, wherein said solid particles comprise hydrophilic solid particles.
65. The method of claim 62, wherein said solid particles are added to said oil at a treat rate of about 0.05wt% to about 0.25wt% based on the weight of said oil.
- 10 66. The method of claim 41, wherein said pretreating step comprises photochemically treating said oil prior to emulsification.
67. The method of claim 66, wherein said step of photochemically treating said oil comprises irradiating said oil.
68. The method of claim 67, wherein said step of irradiating said oil comprises exposing said oil to radiation in the range of ultraviolet to visible radiation.
- 15 69. The method of claim 67, wherein said step of irradiating said oil comprises exposing said oil to sunlight.
70. The method of claim 66, wherein said photochemical treatment is enhanced by the addition of a dye sensitizer.
- 20 71. The method of claim 66, wherein said method further comprises the addition of solid particles to said oil prior to emulsification to further enhance the stability of said emulsion.
72. The method of claim 71, wherein said solid particles are added to said oil before said photochemical treatment step.

73. The method of claim 71, wherein said solid particles are added to said oil after said photochemical treatment step, and before said emulsification.
74. The method of claim 71, wherein said solid particles comprise hydrophobic solid particles.
- 5 75. The method of claim 71, wherein said solid particles comprise hydrophilic solid particles
76. The method of claim 71, wherein said solid particles are added as a gel comprising solid particles and water.
- 10 77. The method of claim 76, wherein said solid particles comprise about 1 wt% to about 30 wt% of said gel based on the weight said water.
78. The method of claim 71, wherein said gel is added to said oil in a treat range of about 5 wt% to about 95 wt% of said gel to said oil.
79. The method of claim 76, wherein said solid particles are bentonite clay.
- 15 80. The method of claim 71, wherein said solid particles are added to said oil at a treat rate of about 0.05wt% to about 2.0wt% based on the weight of said oil.
81. The method of claim 41, wherein said water-in-oil emulsion is used as a drive fluid to displace hydrocarbons in said subterranean formation.
82. The method of claim 41, wherein said water-in-oil emulsion is used as a barrier fluid to divert the flow of hydrocarbons in said subterranean formation.
- 20 83. A water-in-oil emulsion for use in recovering hydrocarbons from a subterranean formation, said emulsion comprising
- (a) oil, wherein at least a portion of said oil is pretreated by at least one of the steps of adding a polymer to said oil, biotreating said oil, photochemically treating said oil, or combinations thereof; and



(b) water droplets suspended in said oil.

84. The emulsion of claim 83, further comprising solid particles which are insoluble in said oil and said water at the conditions of said subterranean formation.